DESCRIPTION

CHEMICAL REACTION SYSTEM OF ELECTROCHEMICAL CELL TYPE,

METHOD FOR ACTIVATION THEREOF AND METHOD FOR REACTION

TECHNICAL FIELD

The present invention relates to an electrochemical cell-type chemical reaction system, and more specifically relates to a chemical reaction system which efficiently excludes nitrogen oxides from exhaust gas containing oxygen. The present invention is useful in that it provides a novel chemical reactor which has micro reaction regions for performing oxidation and reduction reactions on a target substance introduced into part of the chemical reaction part of the aforementioned chemical reaction system so that oxygen and nitrogen oxides are separated and adsorbed from exhaust gas by particular structures within the aforementioned micro reaction regions, thus allowing a target substance to be efficiently processed with low electric power consumption.

Moreover, the present invention relates to an energy-saving electrochemical reaction system and an activation method therefor, and relates more particularly to a chemical reaction system which efficiently excludes nitrogen oxides from exhaust gas containing oxygen for example, and to a

method of use and activation method therefor. The present invention is useful in that it provides a new chemical reaction system, along with a method of use and an activation method therefor, wherein when reactivity has been reduced by adsorption of oxygen atoms on the surface during exclusion of nitrogen oxides from exhaust gas in the electrochemical reaction system, the aforementioned chemical reaction system can be reactivated with low power consumption, thus allowing efficient chemical reaction of the target substance.

Moreover, the present invention relates to a reaction method using an oxidation-reduction reactor, and relates more particularly to a chemical reaction method of oxidizing organic matter, organochlorine compounds, hydrogen, carbon monoxide, nitrogen oxides, ammonia and the like for example or a chemical reaction method of reducing organic matter, oxygen, water, nitrogen oxides and the like using an oxidation-reduction reactor composed of a solid electrolyte which is an oxygen ion conductor and at least an electrode consisting of an electron conductor. The present invention is useful in that it provides a method of removing nitrogen oxides from the exhaust gas of burners and the like for example using the aforementioned oxidation-reduction reactor.

BACKGROUND ART

At present, the principal method of excluding nitrogen oxides produced by gasoline engines is with ternary catalysts. However, because the exhaust gas from lean burning engines and diesel engines, which allow improved fuel consumption, contains an excess of oxygen, reduction of catalytic activity due to adsorption of oxygen by the surface of the ternary catalyst is a problem, preventing exclusion of nitrogen oxides.

On the other hand, by applying a flow of current to a solid electrolyte film having oxygen ion conductivity removal is also accomplished without causing adsorption of oxygen from the exhaust gas by a catalyst surface. One proposal for a catalytic reactor is a system which simultaneously removes surface oxygen and breaks down nitrogen oxides into oxygen and nitrogen by applying voltage to a solid electrolyte sandwiched between electrodes on both sides.

However, the problem is that in the aforementioned method if there is an excess of oxygen in the exhaust gas, because the adsorption and decomposition reaction sites of the coexisting oxygen and nitrogen oxides consist of the same oxygen defects, the adsorption probability of the nitrogen oxides is much lower than that of the oxygen

3

molecules for reasons of both molecular selectivity and coexisting molecular ratios, so that a large flow of current is required to break down the nitrogen oxides, greatly increasing electric power consumption.

Under these circumstances, the present inventors have already discovered that in a chemical reactor it is possible to efficiently process a target substance with low electric power consumption by making the internal structure of the cathode a structure in which nanometer-sized through holes are wound through the top of the same layer, and an electron conductor and an ion conductor on a scale of nanometers to less than a micron are distributed together in a dense network, thus reducing the excess oxygen which is an interfering gas during chemical reaction of the target substance (Japanese Patent Application No. 2001-225034). However, because in this method residual oxygen molecules in the treated gas which have passed through the upper part of the same layer are still more selectively adsorbed and degraded in the reaction sites than are the nitrogen oxides, the reduction in energy consumption is inadequate.

Moreover, another problem with this method is that the reduction in energy consumption is inadequate because current needs to be supplied continuously in order to remove coexisting oxygen molecules.

4

On the other hand, a variety of catalysts are often used in chemical reactions and oxidation-reduction reactions in particular, including homogenous catalysts and heterogenous catalysts. Compared to homogenous catalysts, heterogenous catalysts which used solid catalysts such as precious metals and zeolites offer the advantage of easy separation of the reactant from the catalyst. However, although heterogenous catalysts allow easy separation of the catalyst, because the raw material and the reactant occupy the same space the necessary product is separated and purified from unreacted raw material and by-products. A method which has been studied which does not require such separation and purification is one employing a reaction separation membrane (*Kagaku Sosetsu* No. 41, "Design of high function catalysts," Japan Chemical Society (1999), p. 131).

In a method employing a reaction separation membrane, for example when synthesizing ethane by an oxygen coupling reaction of methane using an oxygen permeable membrane ($3CH_4 + 1/2\ O_2 \rightarrow C_2H_4 + H_2O$), CH_4 and O_2 are separated by the oxygen permeable membrane and a suitable catalyst is placed on the wall of the permeable membrane on the CH_4 side to make a CH_4/catalyst/oxygen permeable membrane/O_2 system, and O_2 is activated on the catalyst through the oxygen permeable membrane to selectively synthesize ethane. When the same

5

reaction is performed using a hydrogen permeable membrane, the hydrogen permeable membrane is of course placed between the CH_4 and O_2 in a CH_4/catalyst/hydrogen permeable membrane/O_2 system, but a catalyst having methane dehydrogenation activity needs to be placed on the wall of the permeable membrane. Membranes used as reaction separation membranes are generally classified into porous membranes, metal membranes, ion conductor membranes, mixed conductor membranes and the like according to the permeation mechanism of the substance permeated. Porous membranes which allow selective permeation of molecules include zeolites and other having nanopores, but synthesis of dense zeolite membranes without pinholes has not been established.

Of the metal membranes, Pd membranes and Pd-Au alloy membranes are used as reaction separation membranes. Both are used as hydrogen reaction separation membranes (hydrogen permeable membranes). The concentration difference (hydrogen partial pressure difference) between the two sides of the membrane is used as the drive force of a hydrogen permeable membrane. Ion conductor membranes (electrolyte membranes) are primarily hydrogen ion conductors and oxygen ion conductors. When an ion conductor membrane is used as a reaction separation membrane, because the drive force conducted by the ions is a field gradient electrodes are

6

installed on both sides of the membrane and the electrodes are electrically connected to each other with electrical wires. A movement of electrons through the lead wire (external circuit) occurs because the ions pass through the membrane while at the same time neutralizing electric charge. In a mixed conductor membrane, because both ions and electrons (or electron holes) can be conducted through the membrane there is no need for electrodes and lead wires to send the electrons. However, the concentration difference between the two sides of the membrane is used as the ion drive force.

In particular, in a reaction separation membrane employing an ion conductor membrane, because the field gradient is the drive force a reaction can proceed irrespective of the concentration difference. Electrodes are required, however, and a stable substance having electron conductivity which is inactive in oxidation and reduction reactions is used for the electrodes. For example, precious metals such as Pt, Pd and the like, carbon, and in oxidizing atmospheres $LaCoO_3$, $LaFeO_3$, $LaMnO_3$, $LaCrO_3$ and other electron conducting oxides and the like are used. In one example of a reaction separation membrane employing a hydrogen ion conductor membrane, trace acetylene is selectively removed by hydrogenation from ethylene. A

7

reactor such as a C_2H_4, C_2H_2/Cu electrode/hydrogen ion conductor membrane/Pt black electrode/H_2 reactor is constructed, and electricity is applied between the two electrodes to selectively hydrogenate (reduce) acetylene, so that acetylene present as an impurity in the ethylene is converted to ethylene and removed. Such a reaction occurs because of the strong affinity between acetylene and the Cu electrode and the occurrence of atomic hydrogen sent through the hydrogen ion conductor membrane.

In one example of a reaction separation membrane employing a solid electrolyte membrane having oxygen ion conductivity, nitrogen oxides are removed by reduction from exhaust gas. One reactor which has been proposed is a system developed to simultaneously remove surface oxygen and break down nitrogen oxides into oxygen and nitrogen by applying voltage to a solid electrolyte sandwiched between electrodes on both sides. To present the related background art, in the literature of background art it has been proposed that platinum electrodes be formed on both sides of zirconia stabilized with scandium oxide, and voltage applied to break down into nitrogen oxides and oxygen (*J. Electrochemical Soc.* 122, 869 (1975)). In the literature of background art it has also been proposed that palladium electrodes be formed on both sides of zirconia stabilized

8

with yttrium oxide, and voltage applied to break down into nitrogen and oxygen in a mixed gas of nitrogen oxides, hydrocarbons and oxygen (*J. Chem. Soc. Faraday Trans.* 91, 1995 (1995)). In this way, in a reaction separation membrane in which an ion conductor membrane is provided with electrodes and voltage is applied between the electrodes with the field gradient as the drive force, not only can the reaction proceed independently of the concentration difference of the reactant or product, but the types of ions passing through the ion conductor membrane are activated on the electrode and molecules are easily degraded at the interface between ion conductor and electrode, so that oxidation and reduction can be easily performed.

However, in a reaction method using a reaction separation membrane in which an ion conductor membrane is provided with electrodes and voltage is applied between the electrodes with the field gradient as the drive force, oxidation and reduction ability is high but selectivity is low. For example, when removing nitrogen oxides by reduction in a reactor in which the aforementioned ion conductor is provided with electrodes, if oxygen molecules are present they are also broken down into oxygen ions, reducing the efficiency of the reduction removal of nitrogen oxides which is the objective of exhaust gas purification.

9

Moreover, while a simple oxidation-reduction reaction using a reducing agent or oxidizing agent with suitable selectivity is also possible, in this case the reducing agent or oxidizing agent needs to be supplied or replaced because the reaction cannot continue once this has been exhausted.

DISCLOSURE OF THE INVENTION

Therefore, in light of the aforementioned background art the inventors arrived at the present invention as a result of exhaustive research into solving these various problems when they discovered that a reaction could be made more efficient by forming pairs of reaction sites for performing simultaneous reduction reactions in a chemical reaction part (for example, a working electrode layer located on the upper part of a cathode) and exploiting the selective adsorbability of each for oxygen molecules and nitrogen oxides.

That is, it is an object of the first embodiment of the present invention to solve the aforementioned problems of background art and provide a chemical reactor capable of efficiently excluding nitrogen oxides with low power consumption wherein the amount of current required to break down nitrogen oxides is reduced by using pairs of adsorbent

10

substances which are selective for oxygen molecules and
nitrogen oxide molecules to facilitate absorption of
nitrogen oxides when excess oxygen is present in exhaust gas.

Moreover, in light of the aforementioned background art
the inventors arrived at the present invention as a result
of exhaustive research aimed at solving these various
problems when they discovered that it was possible to ionize
and remove oxygen molecules and reactivate the system by
forming, in a working electrode layer located in the upper
part of a cathode in the chemical reaction part, local
reaction sites which allow greater efficiency of the
chemical reaction by performing oxygen adsorption and
adsorption-reduction reactions of nitrogen oxides
simultaneously, and by further applying current to the
chemical reaction system after adsorption of a fixed amount
of oxygen molecules.

That is, it is an object of the second embodiment of
the present invention to solve the aforementioned problems
and provide a chemical reaction system in which the amount
of current required to break down nitrogen oxides is reduced
by facilitating absorption of nitrogen oxides by means of
pairs of substances with selective adsorbency for oxygen
molecules and nitrogen oxide molecules when excess oxygen is
present in exhaust gas, and in which the chemical reaction

system is reactivated at the same time by application of current after adsorption of a fixed amount of oxygen, and which is capable of efficiently excluding nitrogen oxides with low power consumption.

Moreover, it is an object of the third embodiment of the present invention, which was developed with the aim of establishing a new reaction method in an oxidation-reduction reactor capable of solving the aforementioned problems of background art, to provide a novel reaction method wherein oxidation or reduction can be achieved with high selectivity using an oxidation-reduction reactor without the need for supplying or exchanging a reducing agent or oxidizing agent.

Next, the first embodiment of the present invention is explained in more detail.

The present invention relates to a chemical reaction system for performing chemical reactions of a target substance, and this chemical reaction system consists of a chemical reaction part in which the aforementioned chemical reactions of the aforementioned target substance are performed, and preferably of a barrier layer for impeding ionization of oxygen.

The chemical reaction part for performing chemical reactions of a target substance .is preferably provided with

a reduction phase which produces ions by supplying electrons to elements contained in the target substance, an ion conduction phase which conducts ions from the reduction phase, and an oxidation phase which discharges electrons from ions conducted by the ion conduction phase.

In the present invention, the target substance is preferably nitrogen oxides in exhaust gas, and the nitrogen oxides are reduced in the reduction phase to generate oxygen ions which are conducted in the ion conduction phase. However, the target substance in the present invention is not limited to nitrogen oxides. In the chemical reactor of the present invention carbon dioxide can be reduced to produce carbon monoxide, a mixed gas of hydrogen and carbon monoxide can be produced from methane, or hydrogen can be produced from water.

The chemical reaction system can be in the form of a pipe, plate, honeycomb or the like for example, but in particular it preferably has one or multiple through holes with a pair of openings (as in a pipe or honeycomb), with chemical reaction sites located in each through hole.

In the aforementioned chemical reaction, the reduction phase is porous and should selectively adsorb the substance which is the target of the reaction. Because in reduction electrons are supplied to elements contained in the target

13

substance to generate ions which are transmitted to the ion

conduction phase, it preferably consists of an electrically

conductive substance. For purposes of promoting

transmission of electrons and ions, it is desirable that it

consist of a mixed conductive substance which has the

features of both electron conduction and ion conduction, or

that it consist of a mixture of an electron conductive

substance and an ion conductive substance. The reduction

phase may have a layered structure of at least two or more

phases of these substances.

There are no particular limits on the electrically

conductive substance and ion conductive substance used as

the reduction layer. For example, platinum, palladium and

other precious metals as well as nickel oxide, cobalt oxide,

copper oxide, lanthanum manganite, lanthanum cobaltite,

lanthanum chromite and other metal oxides can be used as the

electrically conductive substance. Barium-containing oxides,

zeolites and the like which selectively adsorb the target

substance can also be used as the reduction layer.

Preferably, at least one or more of the aforementioned

substances is used as a mixture with at least one or more

ion conductive substances. Ion conductive substances which

can be used include for example zirconia stabilized with

yttria or scandium oxide and ceria, lanthanum gallate or the

14

like stabilized with gadolinium oxide or samarium oxide. It is also desirable that the reduction layer consist of a layered structure of at least two or more phases of the aforementioned substances. More preferably, the reduction layer consists of a layered structure of two phases, an electrically conductive phase consisting of a precious metal such as platinum or the like and a mixed phase of nickel oxide and zirconia stabilized with yttria or scandium oxide.

The ion conduction phase consists of a solid electrolyte having ion conductivity, and preferably consists of a solid electrolyte having oxygen ion conductivity. Examples of solid electrolytes having oxygen ion conductivity include zirconia stabilized with yttria or scandium oxide and ceria or lanthanum gallate stabilized with gadolinium oxide or samarium oxide, but these are not limitations. It is preferable to use zirconia stabilized with yttria or scandium oxide, which has excellent long-term stability, high conductivity and strength.

The oxidizing phase contains a conductive substance for purposes of causing electrons to be released from ions from the ion conduction phase. For purposes of promoting transmission of electrons and ions it is desirable that it consist of a mixed conductive substance having the features of both electron conductivity and ion conductivity or of a

15

mixture of an electron conductive substance and an ion conductive substance. There are no particular limits on the electrically conductive substance and ion conductive substance used as the oxidizing phase. For example, platinum, palladium and other precious metals as well as nickel oxide, cobalt oxide, copper oxide, lanthanum manganite, lanthanum cobaltite, lanthanum chromite and other metal oxides can be used as the electrically conductive substance. For the ion conductive substance, zirconia stabilized with yttria or scandium oxide or ceria or lanthanum gallate stabilized with gadolinium oxide or samarium oxide can be used for example.

In order to prevent a supply of electrons necessary for producing oxygen ions when oxygen molecules have been surface adsorbed, the barrier layer has a material and structure which inhibit electrons supplied by the chemical reaction part and particularly the reduction phase from arriving at the surface. This barrier layer is preferably an ion conductor, mixed electrical conductor or insulator, and when it is a mixed electrical conductor the proportion of electron conductivity is preferably extremely small because when electron conductivity is high the inhibitory effect on electron conduction is reduced.

A feature of the present invention features is that micro reaction regions where oxidation-reduction reactions

16

of a target substance take place are introduced into part of the chemical reaction part by applying current or an electrical field or heat treatment in a reducing atmosphere or under reduced pressure to the point of contact between the ion conduction phase and the electron conduction phase, which is composed of a combination of any of an ion conductor, an electron conductor and a mixed electrical conductor. In the present invention, features include the formation as the aforementioned micro reaction regions of interfaces consisting of metal phases of the electron conduction phase, oxygen deficient parts of the ion conduction phase and micro spaces (gaps) surrounding the contacts of these at the points of contact between the electron conduction phase and the ion conduction phase, the introduction into the cathode of the aforementioned micro reaction regions where the aforementioned oxidation-reduction reactions take place, the formation in the top part of the cathode of a working electrode layer for managing oxidation-reduction reactions, and the introduction into the same layer of micro reactions regions nanometers to a micrometer in size where the aforementioned oxidation-reduction reactions take place.

The working electrode located in the top part of the cathode within the chemical reaction part has a structure

which allows adsorption of oxygen molecules and adsorption

of a target substance to be performed simultaneously by

separate substances suited to each reaction, in addition to

the highly efficient adsorption and degradation of a target

substance discovered previously (Japanese Patent Application

No. 2001-225034). That is, as shown for example in Figure 2,

a metal phase produced by reduction of oxides or present

from the beginning (preferably in the form of ultrafine

particles (diameter roughly 10 nm to 100 nm) to obtain high

reactivity) comes into contact with an oxygen deficient part

of a neighboring ion conduction phase and micro spaces a few

nm to a few tens of nm or less in size are created around

these points of contact, so that oxygen molecules in the

introduced target gas and the target substance itself are

each selectively adsorbed and broken down in the oxygen

deficient part and the metal phase, respectively, and power

consumption is greatly reduced. If the spaces around the

contact points are larger than a few tens of nm, they will

be larger than the mean free paths of the gas molecules, and

the separation and adsorption effect will gradually decline,

or if the formed regions around the contact points are

larger than 100 nm, that is if they are sufficiently larger

than the Debye length and the diffusion length of the oxygen

defect, the selective separation and exclusion performance with respect to the target gas will be diminished.

The metal phase and oxygen deficient partly normally form contacts because of their production mechanisms, but it is not absolutely necessary for them to contact in order for the aforementioned selective separation function to apply. That is, even if the oxygen deficient part which is formed as a result movement of oxygen in the ion conduction phase due to contribution of electrons from the metal phase (oxide phase before reaction) when current is applied loses contact with the metal phase due to effects such as heat shrinkage after formation thereof, this is not a serious impediment to the selective separation function of the target gas which is the effect of the present invention.

Such a structure is formed by subjecting the chemical reaction system to current or to heat treatment in a reducing atmosphere or under reduced pressure in addition to the heat treatment processes necessary for forming the structure discovered previously (heat treatment in atmosphere at 1400 to 1450°C in a zirconia-nickel oxide system). That is, a necessary condition for the aforementioned structure is the formation of a reduction phase by application of current at a high temperature of a few 100°C or more or heat treatment under reduced pressure

19

or in a hydrogen atmosphere or other reducing atmosphere using an oxide which is relatively easy to reduce.

In this step, the simultaneous formation of ultrafine structures which are desirable for efficient reactions occurs more favorably when current is applied. This includes the production due to volume changes in the crystal phase from the oxidation-reaction of nanometer to micrometer sized holes suited for introduction of the target gas, the formation of ultrafine particle due to re-crystallization of the reduction layer, the formation of oxygen deficient parts in the ion conduction phase throughout the oxidation-reduction reaction and the like.

The substances which make up such a structure may be a combination of an ion conduction phase and an electron conduction phase, a mixture of conductive phases or a combination of this with an ion conduction phase or electron conduction phase. When the target substance is nitrogen oxides, a nickel or other metal phase is desirable as the reduction phase because it exhibits highly selective adsorption.

In the present invention, substnces which constitute all or part of the aforementioned micro reaction regions have oxidizing and reducing effects on the target substance. The aforementioned metal phase consists for example of

ultrafine particles of a metal phase produced by an oxidation-reduction reaction generated across some or all of an electron conductor or mixed electrical conductor when the aforementioned chemical reaction system is subjected to current or heat treatment in a reducing atmosphere. Moreover, the aforementioned oxygen deficient part consists of an oxygen deficient layer produced by an oxygen-reduction reaction generated in some or all of an ion conductor or mixed electrical conductor when the aforementioned chemical reaction system is subjected to current or heat treatment in a reducing atmosphere. The aforementioned micro reaction regions have a structure in which the ion conductor and electron conductor contact each other directly in at least one place, or contact each other during the manufacturing process.

The chemical reaction system of the present invention can be prepared by subjecting the contact points in the aforementioned chemical reaction part of the ion conduction layer and the electron conduction layer, which are composed of a combination of any of an ion conductor, an electron conductor and a mixed electrical conductor, to current or to heat treatment in a reducing atmosphere or under reduced pressure so as to introduce into the aforementioned chemical reaction part micro reaction regions in which oxidation-

21

reduction reactions of the target substance take place. It
is desirable when constructing the interfaces of the
aforementioned substances that one or both be in a reduced
state.

It is desirable in the present invention that the
aforementioned chemical reaction be a conversion reaction of
matter or energy, that the aforementioned target substance
be nitrogen oxides, that the aforementioned chemical
reaction be reduction degradation of nitrogen oxides, and
that the aforementioned chemical reaction be represented by
the general formula:

$Mox + xe \rightarrow M + x/2O^{2-}$

$M \rightarrow xe + M^{x+}$
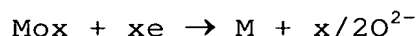
(where M is a metal, O is an oxygen atom and e is an
electron)

Next, the second embodiment of the present invention is
explained in more detail.

The present invention relates to a chemical reaction
system for performing chemical reaction of a target
substance, with this chemical reaction system being composed
of a chemical reaction part where the aforementioned
chemical reaction of the aforementioned target substance

22

proceeds and preferably of a barrier layer for impeding ionization of oxygen.

The chemical reaction part for performing chemical reactions of a target substance ideally has a reduction phase which supplies electrons to elements contained in the target substance to generate ions, an ion conduction phase which conducts ions from the reduction phase, and an oxidation phase which releases electrons from ions conducted by the ion conduction phase, but apart from these it is possible as appropriate to use as basic units oxidizing and/or reducing catalysts having functions equivalent to these, namely oxidation catalysts, reduction catalysts or oxidation-reduction catalysts. In this case, there are no particular limits on these constituent elements.

In the present invention the target substance is preferably nitrogen oxides in exhaust gas, and nitrogen oxides are reduced in the reduction phase, producing oxygen ions which are conducted in the ion conduction phase. However, the target substance in the present invention is not limited to nitrogen oxides. The chemical reactor of the present invention can be applied to producing carbon monoxide by reduction of carbon dioxide, producing a mixed gas of hydrogen and carbon monoxide from methane or producing hydrogen from water.

The chemical reaction system may be in the form of a pipe, plate or honeycomb for example, but in particular it preferably has one or multiple through holes with a pair of openings (as in a pipe or honeycomb), with chemical reaction sites located in each through hole.

In the aforementioned chemical reaction part, the reduction phase is porous and should selectively adsorb the substance which is the target of the reaction. Because in reduction electrons are supplied to elements contained in the target substance to generate ions which are transmitted to the ion conduction phase, it preferably consists of an electrically conductive substance. For purposes of promoting transmission of electrons and ions, it is desirable that the reduction phase consist of a mixed conductive substance which has the features of both electron conduction and ion conduction, or that it consist of a mixture of an electron conductive substance and an ion conductive substance. The reduction phase may have a layered structure of at least two or more phases of these substances.

There are no particular limits on the electrically conductive substance and ion conductive substance used as the reduction layer. For example, platinum, palladium and other precious metals and nickel oxide, cobalt oxide, copper

oxide, lanthanum manganite, lanthanum cobaltite, lanthanum chromite and other metal oxides can be used as the electrically conductive substance. Barium-containing oxides, zeolites and the like which selectively adsorb the target substance can also be used as the reduction layer. Preferably, at least one or more of the aforementioned substances is used as a mixture with at least one or more ion conductive substances. Ion conductive substances which can be used include for example zirconia stabilized with yttria or scandium oxide and ceria, lanthanum gallate or the like stabilized with gadolinium oxide or samarium oxide. It is also desirable that the reduction layer consist of a layered structure of at least two or more phases of the aforementioned substances. More preferably, the reduction layer consists of a layered structure of two phases, an electrically conductive phase consisting of a precious metal such as platinum or the like and a mixed phase of nickel oxide and zirconia stabilized with yttria or scandium oxide.

The ion conduction phase consists of a solid electrolyte having ion conductivity, and preferably consists of a solid electrolyte having oxygen ion conductivity. Examples of solid electrolytes having oxygen ion conductivity include zirconia stabilized with yttria or scandium oxide and ceria or lanthanum gallate stabilized

25

with gadolinium oxide or samarium oxide, but these are not limitations. It is preferable to use zirconia stabilized with yttria or scandium oxide, which has excellent long-term stability and is highly conductive and strong.

The oxidation phase contains a conductive substance for purposes of causing electrons to be released from ions from the ion conduction layer. For purposes of promoting transmission of electrons and ions it is desirable that it consist of a mixed conductive substance having the features of both electron conductivity and ion conductivity, or of a mixture of an electron conductive substance and an ion conductive substance. There are no particular limits on the electrically conductive substance and ion conductive substance used as the oxidizing layer. For example, platinum, palladium and other precious metals and nickel oxide, cobalt oxide, copper oxide, lanthanum manganite, lanthanum cobaltite, lanthanum chromite and other metal oxides can be used as the electrically conductive substance. For the ion conductive substance, zirconia stabilized with yttria or scandium oxide or ceria or lanthanum gallate stabilized with gadolinium oxide or samarium oxide can be used for example.

The purpose of the barrier layer is to prevent the supply of electrons necessary for producing oxygen ions when oxygen molecules have been surface adsorbed. Alternatively,

26

it is provided for the purpose of preventing re-oxidation of metals (such as metal nickel) produced by reduction reactions of electrically conductive oxides (such as nickel oxide) by oxygen ions in the chemical reaction part, and has a material and structure to block electrons supplied by the chemical reaction part and particularly the reduction layer from reaching the surface. This barrier layer is preferably an ion conductor, mixed electrical conductor or insulator, and when it is a mixed electrical conductor the proportion of electron conductivity is preferably extremely small because when electron conductivity is high the suppression effect on electron conduction is reduced.

In a chemical reaction system wherein the chemical reaction part is composed of an oxygen ion conductor (ion conduction phase), a paired cathode (reduction phase) and an anode (oxidation phase) with the ion conduction phase therebetween or of an oxidization and/or reduction catalyst as basic units for performing chemical reactions of a target substance, it is a feature of the present invention that the ability to ionize and remove oxygen which impedes reactions when adsorbed by the chemical reaction part is activated either by application of current or an electrical field between the cathode and anode of the aforementioned chemical reaction part, or by heat treatment in a reducing atmosphere

27

or under reduced pressure. In the present invention, favorable examples include the use as the chemical reaction part of a chemical reaction part wherein micro reaction regions where oxidation-reduction reactions of the target substance take place are introduced into part of the chemical reaction part by subjecting the contact points between an ion conduction phase and an electron conduction phase composed of a combination of any of an ion conductor, an electron conductor or a mixed electrical conductor to current or an electrical field or to heat treatment in a reducing atmosphere or under reduced pressure; or the use as the chemical reaction part of a chemical reaction part having a reduction phase which has individual selectivity for both oxygen and the target substance and pores a micrometer or less in size for efficiently supplying and processing the target substance in the reduction phase; or the use of a chemical reaction part wherein interfaces consisting of metal phase parts of the electron conduction phase, oxygen deficient parts of the ion conduction phase and micro spaces (gaps) surrounding the contact points thereof are formed at the contact points between the electron conduction phase and the ion conduction phase as the aforementioned micro reaction regions; or the use as the chemical reaction part of a chemical reaction part wherein

28

micro reaction regions wherein the aforementioned oxidation-reduction reactions take place are introduced into the cathode as the aforementioned chemical reaction part; and also the use as the chemical reaction part of a chemical reaction part having a working electrode layer for performing oxygen-reduction reactions in the upper part of the cathode wherein micro regions nanometers to a micrometer in size wherein the aforementioned oxidation-reduction takes place are introduced into the same layer.

The working electrode located in the top part of the cathode within the chemical reaction part has a structure which allows adsorption of oxygen molecules and adsorption of a target substance to be performed simultaneously by separate substances suited to each reaction, in addition to the highly efficient adsorption and degradation of a target substance discovered previously (Japanese Patent Application No. 2001-225034). That is, a metal phase produced by reduction of oxides or present from the beginning (preferably in the form of ultrafine particles (diameter 10 to 100 nm) to obtain high reactivity) comes into contact with an oxygen deficient part (a region of about 5 nm as estimated by calculating from of the Debye length) of a neighboring ion conduction phase, and micro spaces a few nm to a few tens of nm or less in size are created around these

points of contact, so that oxygen molecules in the
introduced target gas and the target substance itself are
each selectively adsorbed and broken down in the oxygen
deficient part and the metal phase, respectively, greatly
reducing electrical power consumption.

Such a structure is formed by subjecting the chemical
reaction system to current or to heat treatment in a
reducing atmosphere or the like in addition to the heat
treatment processes necessary for forming the structure
discovered previously (heat treatment in atmosphere at 1400
to 1450°C in a zirconia-nickel oxide system). That is, a
reduction phase is formed by application of current under
high temperatures of several 100°C or more using an oxide
which is relatively easy to reduce. In this step, ultrafine
structures are formed which are desirable for efficient
reactions, including the production due to volume changes in
the crystal phase from the oxidation-reduction reaction of
pores nanometers to a micrometer in size which are suitable
for introduction of the target gas, the formation of
ultrafine particles by re-crystallization of the reduction
phase, and the formation of oxygen deficient parts in the
ion conduction phase throughout the oxidation-reduction
reaction. An example of a local structure formed by the
aforementioned methods which is desirable for the inner

structure of the working electrode layer is shown in Figure 4.

Substances which constitute such ultrafine structures are a combination of an ion conduction phase and an electron conduction phase, a mixture of conduction phases or a combination of this with an ion conduction phase or electron conduction phase. When the target substance is nitrogen oxides, a nickel or other metal phase is desirable as the reduction phase because it exhibits highly selective adsorption.

In addition to the method of introducing a reducing agent previously described as background art, a method which has been proposed for reactivating a chemical reaction system is one in which carbon or the like already forms an integrated structure in the chemical reaction system, and the carbon oxidizes during the chemical reaction to reduce the oxidized metal phase (K. Miura et al., *Chemical Engineering Science* 56, 1623 (2001)). However, in these methods reducing agents are required, and since reactivation becomes impossible when the reducing agent is exhausted an electrical reactivation method is more desirable for long term or continuous use of the system.

In the present invention, it is possible to apply current or the like only when the performance of the

31

chemical reaction system has declined in order to ionize and remove by pumping oxygen adsorbed by the oxygen deficient part of the chemical reaction part. Moreover, it is possible to simultaneously reenergize the reduction phase. In this way, the amount of current in the present invention can be much less than the amount of current required for oxygen pumping in conventional electrochemical cell systems.

Reactivation by oxygen pumping in the present invention is performed by applying current, voltage or heat treatment in a reducing atmosphere or the like to the chemical reaction system when the system is at 400 to 700°C. In the present invention, it is desirable to maintain a temperature of 400 to 700°C or raise or lower the temperature within that temperature range in the aforementioned chemical reaction system while applying current or an electrical field between the cathode and anode for 1 minute to 3 hours. In this case, it is desirable to apply current of 5 mA to 1A or voltage of 0.5 V to 2.5 V to generate an electrochemical reaction, and to perform current or electrical field treatment at an oxygen partial pressure of 0% to 21% (in atmosphere). The treatment temperature differs depending on the material and structures which make up the system, but for example a temperature near 560°C is desirable when zirconia stabilized with yttria is used as the solid

electrolyte, and one near 450°C when ceria is used. The present invention provides an activation method for a chemical reaction system wherein the temperature in the aforementioned chemical reaction system is maintained at 500°C or more or raised or lowered within this temperature range and heat treatment is performed in a reducing atmosphere or under reduced pressure.

In addition to the conditions of treatment temperature and component materials, the conditions of amount of applied current, applied voltage, current time and oxygen partial pressure or total pressure in atmosphere are variable. For example, when zirconia stabilized with yttria is used as the electrolyte and nickel oxide and zirconia as the working electrode materials, the ability to break down nitrogen oxides is restored to the level before treatment by applying current of 100 mA, 2 V for 1 hour (oxygen 10%). The degree of deterioration due to oxygen adsorption is about 20% after 100 hours of continuous operation (without current), and performance can be repeatedly restored by the aforementioned current treatment.

Next, the third embodiment of the present invention is explained in more detail.

In the present invention, the solid electrolyte of the oxygen ion conductor is one with conductivity of $10^{-6}\Omega^{-1} \cdot cm^{-1}$ or more at the temperature of use. Under $10^{-6}\Omega^{-1} \cdot cm^{-1}$ conductance is so low that that an oxidized reductant (R) or reduced oxide (RO_x) cannot be electrochemically reduced or oxidized with sufficient speed, and the energy loss due to internal resistance is too great for practical use. Examples of this solid electrolyte of the oxygen ion conductor include ZrO_2, CeO_2, Bi_2O_3 and $LaGaO_3$ oxides. A ZrO_2 oxide can be stabilized with Y, Sc or the like. A CeO_2 oxide can be stabilized with Gd, Sm or the like. Multiple oxygen ion conductors can be used as a composite or laminate. In particular, from the standpoint of stability a ZrO_2 oxide is desirable for removing nitrogen oxides.

Moreover, in the present invention the electrode material consisting of an electron conductor is one having conductivity of $10^{-6}\Omega^{-1} \cdot cm^{-1}$ or more at the temperature of use. Under $10^{-6}\Omega^{-1} \cdot cm^{-1}$ conductance is so low that an oxidized reductant (R) or reduced oxide (RO_x) cannot be electrochemically reduced or oxidized with sufficient speed, and the energy loss due to internal resistance is too great for practical use. Examples of this electrode material consisting of an electron conductor include metals,

34

stainless steel, alloys, electron conductive oxides, graphite, glassy carbon and other carbons and the like. Moreover, specific examples include platinum, palladium and other precious metals and nickel oxide, cobalt oxide, copper oxide, lanthanum manganite, lanthanum cobaltite, lanthanum chromite and other metal oxides. Multiple electron conductors can be used as a composite or laminate. This may also be compounded with the solid electrolyte of the oxygen ion conductor, or a mixed electrical conductor of an oxygen conductor and an electron conductor may be used. In addition, the electrode material may also be compounded with a reductant or oxidant. In particular, from the standpoint of stability Au, Pt, Ag, Pd, a Ni oxide, a Cu oxide, an Fe oxide, a Mn oxide or a combination of these is desirable for purposes of removing nitrogen oxides.

The reductant (R) used in the present invention may be any consisting of a metal or suboxide and having the ability to reduce the oxide AO_x (where x is 1/2 the oxidation number of A) which is the target of the reaction, with no particular limitations, but desirable examples include Mg, Ca and other alkali earth metals, Ti, Cr, Mo, W, Mn, Fe, Co, Ni, Cu, Ag, Zn and other transitional metals, Al, Ga, In, Sn and other metals and Ti (III), V (IV, III, II), Cr (III, II), Mo (IV, III, II), W (V, IV, III, II), Mn (III), Fe (II), Cu

(I) and other suboxides. In particular, from the standpoint
of selective reactivity a suboxide or metal comprising 50%
or more of one or more elements selected from Ni, Cu and Fe
is desirable for removing nitrogen oxides.

The oxide AO_x (where x is 1/2 the oxidation number of
A) which can be reduced by the reaction method of the
oxidation-reduction reactor of the present invention is for
example organic matter containing oxygen, oxygen, water,
nitrogen oxides or the like, and these can be reduced to the
reduced product AO_{x-y} (where $0<y\leq x$) in the oxidation-
reduction reactor. Reduction of the oxide AO_x can proceed
as far as the wholly reduced A (y = x), or the partially
reduced AO_{x-y} ($0<y<x$).

The oxidant (RO_x) used in the present invention can be
any consisting of oxides which is capable of oxidizing the
compound A which is the target of the reaction, without any
particular limitations, and examples include Ti, Cr, Mo, W,
Mn, Fe, Co, Ni, Cu, Ag, Zn, Pd, Pt, Rh, Au, Ir and other
transitional metal oxides and Al, Ga, In, Sn and other metal
oxides. In particular, from the standpoint of selective
reactivity an oxide comprising 50% or more of one or more
elements selected from Ni, Cu, Ag and Pt is desirable for
oxidation reactions of hydrocarbons and organochlorine
compounds.

36

A compound A which can be oxidized by an oxidation method using the oxidation-reduction reactor of the present invention is for example organic matter, an organochlorine compound, hydrogen, carbon monoxide, nitrogen oxides, ammonia or the like, and these can be oxidized into AO_y oxides in the aforementioned oxidation-reduction reactor. In particular, alcohol or carboxylic acid can be partially oxidized from a hydrocarbon such as methane, ethane, propane, butane or the like, and organochlorine compounds such as dioxins can be oxidation degraded. By controlling the reaction conditions including reaction time, applied voltage and the like, it is possible to take oxidation of compound A as far as perfectly oxidized AO_y ($y = x$), or as far as the intermediate partial oxide AO_{x-y} ($0<y<x$).

When the oxidation-reduction reactor used in the present invention is used as a reduction reactor, an arrangement such as reductant (R)/electrode/oxygen ion conductor/electrode is adopted, or when it is used as an oxidation reactor an arrangement such as electrode/oxygen ion conductor/electrode/oxidant (RO_x) is adopted. The reductant (R) and electrode may be a mixed phase of the two, as may the electrode and oxidant (RO_x). In particular, for purposes of removing nitrogen oxides the size of the nitrogen oxide reductant is preferably in the range of 10 nm

37

to 1 μm. Under 10 nm activity is too high and other oxides are reduced, making it difficult to selectively reduce nitrogen oxides. Over 1 μm, the effective surface area of the nitrogen oxide reductant is reduced, and efficient reduction is hard to achieve. Moreover, the layer containing the reductant (R) or the layer containing the oxidant (RO_x) may be a porous body having pores to make the oxidation and reduction reactions more efficient.

The nitrogen oxygen reductant used in the present invention can be manufactured within the oxidation-reduction reactor by bringing one or more oxide electron conductors selected from an Ni oxide, Cu oxide, Fe oxide and Mn oxide into contact with a solid electrolyte oxygen ion conductor, and applying cathode current to the electron conductor to reduce part of the oxide electron conductor. In the oxidation-reduction reactor of the present invention, in order for the reductant R to restore the oxidized RO_y to the original reductant R so as to reduce the oxide AO_x, RO_y can be electrochemically reduced to R by application of current to the electrode, or else in order for the oxidant $R'O_x$ to restore the reduced $R'O_{x-y}$ to the original oxidant $R'O_x$ so as to oxidize the compound A, $R'O_{x-y}$ can be electrochemically oxidized to $R'O_z$ by application of current to the electrode. Restoration of reductant R or oxidant $R'O_x$ by application of

38

current between electrodes can be accomplished during the oxidation-reduction reaction, or restoration by application of current can be performed after a fixed interval.

In the reaction method using the oxidation-reduction reactor of the present invention, the working temperature should be between 300°C and 1000°C so that sufficient conductivity of the solid electrolyte which is the oxygen ion conductor can be obtained, but it is also possible to perform the oxidation-reduction reaction at a low temperature such as room temperature, heating to the aforementioned temperature only when electrochemically restoring reductant R or oxidant $R'O_x$. Because in the present invention the reductant (R) or oxidant (RO_x) used is any material chosen according to the oxidation or reduction potential of the reaction to be performed in the oxidation-reduction reactor, a highly selective reaction can be achieved under conditions suited to the desired reaction.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a block diagram of a chemical reaction system according to one embodiment of the present invention.

Figure 2 shows one example of a local structure which is desirable as the internal structure of the working electrode layer.

39

Figure 3 is a chart in which the relationship between removal performance of nitrogen oxides and amount of applied current in a chemical reaction system according to the present invention is compared with the results of existing research and the performance of a reactor of a previous application of the inventors.

Figure 4 shows one example of a local structure which is desirable as the internal structure of the working electrode layer.

Figure 5 shows how ability to purify nitrogen oxides is restored by application of current.

List of Elements

1   Barrier layer

2   Working electrode layer

3   Cathode (reduction phase)

4   Ion conduction phase

5   Anode (oxidation phase)

6   Chemical reaction part

7   Chemical reaction system

BEST MODE FOR CARRYING OUT THE INVENTION

Examples of the first embodiment of the present invention are explained below using the drawings. Figure 1 is a block diagram of a chemical reaction system according

to one embodiment of the present invention. In chemical reaction part 6 which makes up chemical reaction system 7, working electrode 2, cathode (reduction layer) 3, ion conduction layer 4 and anode (oxidation layer) 5 are arranged in upstream-to-downstream order with respect to the flow of gas which is the target of the reaction, with barrier layer 1 placed upstream therefrom. In other words, the target gas passes through in order from 1 to 5.

Figure 2 shows one example of a micro reaction region of a desirable internal local structure in working electrode layer 2 according to the present invention. A more detailed explanation is given below with nitrogen oxides used as the target substance.

Example 1

Zirconia stabilized with yttria was used as ion conduction phase 4, in a disk form with a diameter of 20 mm and a thickness of 0.5 mm. Reduction phase 3 was a mixed layer of platinum and zirconia, while working electrode layer 2 was a film consisting of a mixture of nickel oxide and yttria-stabilized zirconia. A platinum film was first screen printed to an area of about 1.8 cm^2 on one side of ion conduction phase 4, and formed by heat treatment at 1200°C. A mixed film of nickel oxide and yttria-stabilized

41

zirconia was screen printed on the platinum film with the same area as the platinum film, and formed by heat treatment at 1450°C. The compounding ratio of nickel oxide to yttria-stabilized zirconia was 6:4 mole. Once a platinum film had been screen printed to an area of 1.8 cm^2 on the other side of ion conduction phase 4 having a formed reduction phase, it was formed by heat treatment at 1200°C to make oxidation phase 5. Barrier layer 1 was formed on the upper part of working electrode layer 2 with a thickness of about 3 microns by screen printing and heat treatment at 1400°C using yttria-stabilized zirconia. The temperature was then raised to 650°C as current of 1.2 V to 25 mA was passed applied cathode 3 and anode 5, and maintained for one hour after which the current was stopped and the system cooled.

The method of treating nitrogen oxides with a chemical reaction system of the present invention formed as above is shown below. Chemical reaction system 7 was placed in a target gas, reduction phase 3 and oxidation phase 5 were fixed with platinum wires as lead wires and connected to a direct current source, and direct current voltage was applied to start the flow of current. Evaluation was performed in a reaction temperature range of 500°C to 600°C. Helium balanced model exhaust gas containing 1000 ppm nitrogen monoxide and 2% oxygen was supplied at a flow rate

of 50 ml/min as the target gas. The nitrogen oxide

concentration in the target gas before and after flow to the

chemical reactor was measured by a chemiluminescent NOx

meter, while nitrogen and oxygen concentrations were

measured by gas chromatography. The exclusion rate of

nitrogen oxides was derived from the amount of decrease in

nitrogen oxides, and the current density and electric power

consumption were measured when the exclusion rate reached

50%.

The reaction temperature of the chemical reactor was

raised to 600°C, and current was supplied to the chemical

reaction part. As the amount of current rose the exclusion

rate of the nitrogen oxides also rose, and nitrogen oxides

fell to about 50% when current density was 31 mA/cm^2 and

power consumption was $61mW/cm^2$. In Figure 3, the

performance sequence of a chemical reactor of the present

invention is shown in comparison with the performance of a

reactor of a previous application and the results of

existing research. It is clear from this figure that the

performance of the chemical reactor of the present

application is superior to the results of existing research.

Example 2

In the energizing and heating process of the final stage of preparing a chemical reaction system as in Example 1, four cycles were performed in which current of 1.2 V to 25 mA was supplied between cathode 3 and anode 5 as the temperature was raised to 650°C and maintained for 1 hour after which the current was stopped, followed by gradual cooling, and the relationship between number of cycles and ability to process nitrogen oxides was investigated. With 2 cycles a nitrogen oxide removal rate of 50% was achieved at a current density of 25 mA/cm^2 and an electric energy consumption of 49 mW/cm^2, while with 3 cycles this fell to a current density of 24 mA/cm^2 and an electric energy consumption of 47 mW/cm^2, but with 4 cycles the results were similar to those achieved with 3 cycles.

Example 3

Changes in reactivity in a chemical reaction system prepared as in Example 1 were investigated relative to amount of coexisting oxygen impeding the reaction and concentration of nitrogen oxides which were the target substance. Under the same experimental conditions as in Example 1, current density and electric energy consumption at 50% degradation were measured (a) with the oxygen amount increased from 2% to 10% and (b) with the nitrogen oxide

concentration reduced from 1000 ppm to 500 ppm. The results
were (a) current density 55 mA/cm^2, electric energy
consumption 150 mW/cm^2 and (b) current density 20 mA/cm^2,
electric energy consumption 37 mW/cm^2, respectively, showing
that in the chemical reaction system of the present
invention relative processing ability is improved even with
a large amount of coexisting oxygen, while a dramatic
improvement in performance is seen with respect to a weak
nitrogen oxide concentration.

Examples of the second embodiment of the present
invention are explained below using the figures. Figure 1 is
a block diagram of a chemical reaction system according to
one embodiment of the present invention. In chemical
reaction part 6 which makes up chemical reaction system 7,
the working electrode, cathode (reduction layer), ion
conduction layer and anode (oxidation layer) are arranged in
upstream-to-downstream order from 2 to 5 with respect to the
flow of gas which is the target of the reaction, with
barrier layer 1 placed upstream therefrom. In other words,
the target gas passes through in order from 1 to 5.

A more detailed explanation is given below with
nitrogen oxides used as the target substance.

Example 4

Zirconia stabilized with yttria was used as ion conduction phase 4, in disk form with a diameter of 20 mm and a thickness of 0.5 mm. Reduction phase 3 was a mixed layer of platinum and zirconia, while working electrode layer 2 was a film consisting of a mixture of nickel oxide and yttria-stabilized zirconia. A platinum film was first screen printed to an area of about 1.8 cm^2 on one side of ion conduction layer 4, and formed by heat treatment at 1200°C. A mixed film of nickel oxide and yttria-stabilized zirconia was screen printed on the platinum film with the same area as the platinum film, and formed by heat treatment at 1450°C. The compounding ratio of nickel oxide to yttria-stabilized zirconia was 6:4 mole. Once a platinum film had been screen printed to an area of 1.8 cm^2 on the other side of ion conduction phase 4 having a formed reduction phase, it was formed by heat treatment at 1200°C to make oxidation phase 5. Barrier layer 1 was formed on the upper part of working electrode layer 2 with a thickness of about 3 microns by screen printing and heat treatment at 1400°C using yttria-stabilized zirconia. The temperature was then raised to 650°C as current of 1.2 V to 25 mA was passed between cathode 3 and anode 5, and retained for one hour after which the current was stopped and the system cooled.

46

The method of treating nitrogen oxides with a chemical reaction system of the present invention formed as above is shown below. Chemical reaction system 7 was placed in a target gas, reduction phase 3 and oxidation phase 5 were fixed with platinum wires as lead wires and connected to a direct current source, and direct current voltage was applied to start the flow of current. System performance with current was evaluated at 600°C, and without current at a reaction temperature of 350°C. Helium balanced model exhaust gas containing 1000 ppm nitrogen monoxide and 2% oxygen was supplied at a flow rate of 50 ml/min as the target gas. The nitrogen oxide concentration in the target gas before and after flow to the chemical reaction system was measured by a chemiluminescent NOx meter, while nitrogen and oxygen concentrations were measured by gas chromatography. The purification rate of nitrogen oxides was derived from the amount of decrease in nitrogen oxides, and the current density and electric power consumption were measured when the purification rate reached 50%.

That is, the chemical reactor was heated to a reaction temperature of 600°C when measurement was initiated, and current was supplied to the chemical reaction part. At this time, the nitrogen oxide purification rate rose as the amount of current increased, and nitrogen oxides decreased

to about 50% when current density was 31 mA/cm^2 and electric power consumption was 61 mW/cm^2.

Current to this chemical reaction system was stopped 1 hour after being initiated, while measurement of the degradation rate of nitrogen oxides was continued. The degradation rate of nitrogen oxides fell about 10% immediately after cessation of current, but then tended to fall slowly, falling only 5% or less after a total of 5 days (120 hours) of continuous measurement, showing that the exclusion rate is reduced over time. When the amount of electric power required for an exclusion reaction of nitrogen oxides over a total of 120 hours was compared with values calculated at an exclusion rate of 35%, it was found that with the present invention it is reduced to about 1/84 or less of that required by continuous current.

Example 5

In order to investigate applicability to conditions of actual use, ability to remove nitrogen oxides was investigated with the oxygen level raised from 2% to 10% and the concentration of nitrogen oxides reduced from 1000 ppm to 500 ppm in a chemical reaction system of the same composition as in Example 4. Current was supplied to the system 3 times for 10 minutes each under the same

temperature and electric power conditions as in Example 4. As shown in Figure 5, the degradation rate of nitrogen oxides decreased 15% or more immediately after initiation of measurement, and had fallen to a nitrogen oxide degradation rate of less than 30% about 20 hours after initiation of measurement, but then decreased gradually and was in rough equilibrium after about 100 hours. After 200 hours, roughly the same changes over time in the nitrogen oxide degradation rate were achieved by once again applying current.

Example 6

Activation of the system by treatment in a reducing atmosphere was evaluated in a chemical reaction system of the same composition as in Example 4. When in a chemical reaction system in which a power consumption of roughly 68 mW/cm^2 was required for 50% nitrogen oxide degradation with 2% coexisting oxygen, a system operating temperature of 650°C and a nitrogen oxide concentration of 1000 ppm, the temperature was raised to 800°C 48 hours after current was stopped (at which point the nitrogen oxide degradation rate had fallen to 38%), a reducing gas of 5% hydrogen, 95% argon was supplied for 10 hours, and nitrogen oxide purification performance was measured, performance was found to have improved by about 2%.

Next, the third embodiment of the present invention is explained in detail based on examples, but the present invention is not limited to these examples alone.

Example 7

Zirconia stabilized with yttrium oxide was used as a solid electrolyte having oxygen ion conductivity, in disk form with a diameter of 20 mm and a thickness of 0.5 mm. The electrode layer was a composite of platinum and zirconia stabilized with yttrium oxide, with a volume ratio of 40:60. The reductant layer was a composite of iron, platinum and zirconia stabilized with yttrium oxide with a volume ratio of 30:30:40 prepared as the upper layer of the aforementioned electrode layer. The electrode layer which was the counter electrode was prepared as a composite of platinum and zirconia stabilized with yttrium oxide with a volume ratio of 60:40 to the same area as the opposite surface of the solid electrolyte disk.

An oxygen reduction reactor prepared in this way was used to synthesize H_2 by reduction of H_2O in the presence of 10% CO_2. By applying current between the electrodes under temperature conditions of 400 to 800°C, it was possible even in the presence of CO_2 to selectively reduce H_2O and manufacture H_2 with a conversion rate of 90%. Moreover,

current was supplied to the electrodes to restore the

reductant, the current was stopped, the same H_2O was

selectively reduced with a conversion rate of 50 to 80% of

H_2, and the reductant was restored by application of current

between the electrodes when the conversion rate fell to 50%

or less. After restoration, the current was stopped and a

reaction was performed as above, and it was possible to

again manufacture H_2 with a conversion rate of 50 to 80%.

Example 8

Zirconia stabilized with yttrium oxide was used as a

solid electrolyte having oxygen ion conductivity, in disk

form with a diameter of 20 mm and a thickness of 0.5 mm.

The electrode layer was a composite of platinum and zirconia

stabilized with yttrium oxide, with a volume ratio of 40:60.

The nitrogen oxide reductant layer was a composite of nickel

oxide and zirconia stabilized with yttrium oxide with a

volume ratio of 40:60 prepared as the upper layer of the

aforementioned electrode layer. The electrode layer which

was the counter electrode was prepared as a composite of

platinum and zirconia stabilized with yttrium oxide with a

volume ratio of 60:40 to the same area as the opposite

surface of the solid electrolyte disk. Current was supplied

between the electrodes at 500°C to reduce some of the nickel

51

oxide of the nitrogen oxide reductant layer into metal nickel particles 100 nm in size and form the final nitrogen oxide reductant layer.

1000 ppm NO as the nitrogen oxides was reduced and removed in the presence of 5% O_2 by an oxidation-reduction reactor prepared in this way. NO was selectively reduced at a conversion rate of 70% even in the presence of O_2 by applying current between the electrodes under temperature conditions of 400 to 700°C. Moreover, current was supplied to the electrodes to restore the reductant, the current was stopped, the same NO was selectively reduced with a conversion rate of 50 to 80%, and the reductant was restored by application of current between the electrodes when the conversion rate fell to 50% or less. After restoration, the current was stopped and a reaction was performed as above, and it was possible to again manufacture NO with a conversion rate of 50 to 80%.

Example 9

Zirconia stabilized with yttrium oxide was used as a solid electrolyte having oxygen ion conductivity, in disk form with a diameter of 20 mm and a thickness of 0.5 mm. The electrode layer was a composite of lanthanum manganite and zirconia stabilized with yttrium oxide, with a volume

ratio of 50:50. The nitrogen oxide reductant layer was a composite of nickel oxide and zirconia stabilized with yttrium oxide with a volume ratio of 40:60 prepared as the upper layer of the aforementioned electrode layer. The electrode layer for the counter electrode was prepared from La-Sr-Ca-Fe-O so as to have the same area as the opposite surface of the solid electrolyte disk. Current was applied between the electrodes at 500°C to convert some of the nickel oxide of the nitrogen oxide reductant layer to metal nickel particles 50 nm in size and form the final nitrogen oxide reductant layer.

1000 ppm NO as the nitrogen oxides was reduced and removed in the presence of 10% O_2 with an oxidation-reduction reactor prepared in this way. It was possible to selectively reduce NO with a conversion rate of 65% even in the presence of O_2 by applying current between the electrodes under temperature conditions of 400 to 700°C. Moreover, current was supplied to the electrodes to restore the reductant, the current was stopped, the same NO was selectively reduced with a conversion rate of 50 to 80%, and the reductant was restored by application of current between the electrodes when the conversion rate fell to 50% or less. After restoration, the current was stopped and a reaction

was performed as above, and it was possible to again manufacture NO with a conversion rate of 50 to 80%.

Example 10

Zirconia stabilized with yttrium oxide was used as a solid electrolyte having oxygen ion conductivity, in disk form with a diameter of 20 mm and a thickness of 0.5 mm. The electrode layer was a composite of platinum and zirconia stabilized with yttrium oxide with a volume ratio of 40:60. The oxidation layer was a composite of silver oxide, platinum and zirconia stabilized with yttrium oxide with a volume ratio of 30:30:40 prepared as the upper layer of the aforementioned electrode layer. The electrode layer which was the counter electrode was prepared as a composite of platinum and zirconia stabilized with yttrium oxide with a volume ratio of 60:40 to the same surface area as the opposite surface of the solid electrolyte disk.

CH_3OH was synthesized by partial oxidation of CH_4 in the presence of 5% CO using an oxidation-reduction reactor prepared in this way. By applying current between the electrodes under temperature conditions of 400 to 600°C, it was possible to manufacture CH_3OH with a conversion rate of 95% by selective oxidation of CH_4 even in the presence of CO. Moreover, current was applied between the electrodes to

restore the oxidant, the current was stopped, the same CH$_4$ was selectively oxidized to manufacture CH$_3$OH with a conversion rate of 60 to 80%, and current was supplied between the electrodes to restore the oxidant when the conversion rate fell to 60% or less. After restoration the current was stopped, and when the same reaction was performed as above it was possible to again manufacture CH$_3$OH with a conversion rate of 60 to 80%.

Example 11

Zirconia stabilized with yttrium oxide was used as a solid electrolyte having oxygen ion conductivity, in disk form with a diameter of 20 mm and a thickness of 0.5 mm. The electrode layer was a composite of platinum and zirconia stabilized with yttrium oxide with a volume ratio of 40:60. The oxidation layer was a composite of copper oxide, platinum and zirconia stabilized with yttrium oxide with a volume ratio of 40:30:30 prepared as the upper layer of the aforementioned electrode layer. The electrode layer which was the counter electrode was prepared as a composite of lanthanum manganite and zirconia stabilized with yttrium oxide with a volume ratio of 60:40 to the same surface area as the opposite surface of the solid electrolyte disk.

Dioxin was oxidation degraded in the presence of 10% CO using an oxidation-reduction reactor prepared as above. By supplying current between the electrodes under temperature conditions of 400 to 600°C, it was possible to selectively oxidize and degrade dioxin with a conversion rate of 80% even in the presence of CO. Moreover, current was applied between the electrodes to restore the oxidant, the current was stopped, the same dioxin was selectively oxidation degraded with a conversion rate of 40 to 70%, and current was supplied between the electrodes to restore the oxidant when the conversion rate fell to 40% or less. After restoration the current was stopped, and when the same reaction was performed as above it was possible to again oxidation degrade dioxin with a conversion rate of 40 to 70%.

Example 12

A CeO_2 oxide stabilized with Sm was used as a solid electrolyte having oxygen ion conductivity, in disk form with a diameter of 20 mm and a thickness of 0.5 mm. The electrode layer was a composite of lanthanum manganite and CeO_2 oxides stabilized with Sm, with a volume ratio of 50:50. The oxidizing layer was a composite of silver oxide, tungsten oxide and CeO_2 oxides stabilized with Sm with a volume ratio of 20:20:30:30, prepared as the upper layer of

the aforementioned electrode layer. The electrode layer

which was the counter electrode was prepared as a composite

of lanthanum manganite and $CeO2_2$ oxides stabilized with Sm

with a volume ratio of 60:40 to the same area as the

opposite surface of the solid electrolyte disk.

CH_3COOH was synthesized by partial oxidation of CH_3CH_2OH

in the presence of 5% CH_4 using an oxidation-reduction

reactor prepared as above. By applying current between the

electrodes under temperature conditions of 400 to 600°C, it

was possible to manufacture CH_3COOH with a conversion rate

of 70% by selective partial oxidation of CH_3CH_2OH even in

the presence of CH_4. Moreover, current was applied between

the electrodes to restore the oxidant, the current was

stopped, the same CH_3CH_2OH was selectively partially

oxidized to manufacture CH_3COOH with a conversion rate of 50

to 70%, and current was supplied between the electrodes to

restore the oxidant when the conversion rate fell to 50% or

less. After restoration the current was stopped, and when

the same reaction was performed as above it was possible to

again manufacture CH_3COOH with a conversion rate of 50 to

70%.

INDUSTRIAL APPLICABILITY

As discussed above, the following effects are achieved by the first embodiment of the present invention.

(1) A chemical reaction system can be provided which is capable of efficiently processing a target substance even in the presence of excess oxygen which interferes with chemical reaction of the target substance.

(2) The amount of current necessary to degrade nitrogen oxides can be reduced, and nitrogen oxides can be efficiently excluded with low electric power consumption.

(3) Micro reaction regions where oxidation and reduction reactions of a target substance take place can be introduced into part of the chemical reaction part of the aforementioned chemical reaction system.

(4) A chemical reaction system can be provided having a chemical reaction part wherein interfaces consisting of metal phase parts of the electron conduction phase, oxygen deficient parts of the ion conduction phase and micro spaces (gaps) surrounding the contact points thereof are formed at the contact points between the electron conduction phase and the ion conduction phase.

Moreover, the following effects are achieved by the second embodiment of the present invention.

(1) A chemical reaction system can be provided capable of efficiently processing a target substance with low

58

electric power consumption even in the presence of excess

oxygen which interferes with chemical reaction of the target

substance.

(2) Nitrogen oxides can be excluded efficiently with

low electric power consumption.

(3) The chemical reaction system can be reactivated.

(4) An energy-saving electrochemical reaction system

can be provided wherein the chemical reaction part can be

reactivated and used by applying current or an electrical

field at intervals of time.

Moreover, embodiment 3 of the present invention relates

to a reaction method for oxidation and reduction reactions,

and the effects described below are achieved by the present

invention.

(1) A reaction method can be provided for oxidizing or

reducing with high selectivity using an oxidation-reduction

reactor without the need of a supply or exchange of a

reducing agent or oxidizing agent.

(2) Because in the reaction method using the

oxidation-reduction reactor of the present invention the

reductant or oxidant is selected according to the reaction

from various substances having oxidizing or reducing ability,

a desired substance such as organic matter, an

organochlorine compound, hydrogen, carbon monoxide, nitrogen

59

oxides, ammonia, nitrogen oxides or the like can be oxidized with high selectivity.

(3) The present invention can be used for example to synthesize useful substances such as hydrogen, methanol, acetic acid and the like, to remove impurities, and to remove harmful substances such as dioxins and nitrogen oxides in exhaust gas.

(4) Since in the method of the present invention the reductant or oxidant can be restored by application of current, a low-maintenance reaction method can be provided wherein these do not need to be exchanged.